Comment on "X-Ray Anomalous Scattering Study of a Charge-Ordered State in NaV_2O_5"

The determination of the charge ordering pattern in the inorganic compound α'-NaV_2O_5 has attracted a lot of attention and there has been quite a number of attempts, both theoretically and experimentally. As the experimental probes (Raman and neutron scattering, x-ray diffraction, NMR, EPR, etc.) do not directly couple with the charges, the conclusions are often contradictory. In particular, it is difficult to disambiguate the charge ordering from a concomitant lattice distortion. The paper by Nakao *et al.* [1] tries to shed light onto the charge ordering problem in α'-NaV_2O_5, as x-ray anomalous scattering is one of the very few experimental techniques that may give access to the charge distribution itself. The key point is the understanding of the energy dependence of two superlattice reflections which at the very bottom comes to estimate how reliable are the values of the anomalous scattering factors, $f(V^{4+})$ and $f(V^{5+})$.

(i) α'-NaV_2O_5 turns out to have two parent compounds, V_2O_5 and CaV_2O_5, with the same crystal structure but with vanadium in different valence states. One first point that the authors have omitted in their reasoning is that the V-O distances between the two compounds are slightly different, and therefore their corresponding f reflect the charge ordering as well as the concomitant lattice distortion. The use in Eq. (1) in [1] of the same anomalous scattering factor to represent an *only charge ordering term* $\{c(\mathbf{Q})\delta_c[f(V^{4+}) - f(V^{5+})]\}$ and those involving both charge ordering and lattice distortion is misleading at best.

(ii) Though not explicitly written in the paper, f'' spectrum shown in Fig. 2 of Ref. [1] seems to have been recorded with powder samples, and therefore corresponds to an average of all crystallographic orientations. This approximation of the tensor properties of the anomalous scattering factor is bound *not* to work in this compound due to the strong anisotropy of the V environment. To illustrate this effect we show in the figure the fluorescence spectra at two different values of the azimuthal angle, ψ. $\psi = 0$ means that the incident polarization (ϵ) is set parallel to the c axis, whereas $\psi = 90$ corresponds to the case $\epsilon \parallel b$. Analogous spectra have been calculated for V_2O_5 [2] with identical conclusions: the prepeak at $E = 5.47$ keV comes from the short V-O bond length which is directed along the c-axis joint to the strong asymmetry of the V environment. The rest of the DANES spectra also shows distinctive features related to the polarization that do not appear in the powder average absorption spectra.

(iii) The analysis of the measured Bragg reflections, $(15/2, 1/2, 1/4)$ and $(13/2, 1/2, 1/4)$, within the framework of zigzag model 2 (which corresponds to an actual crystallographic space group, $Fmm2$) should be revised as the contribution of vanadium atoms located at positions $16e$ to the structure factor of this family of reflections is strictly null. In other words, these reflections do not contain any information on the charge state of the vanadium atoms.

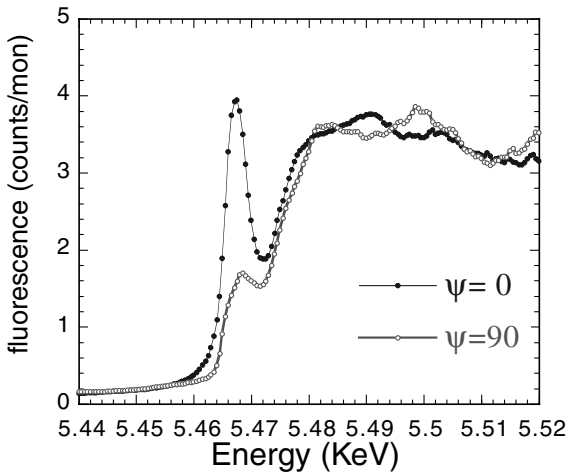

FIG. 1. Fluorescence spectra taken at analogous experimental condition for the $(15/2, 1/2, 1/4)$ reflection. The scattering angle for the fluorescence spectra is $\theta = \theta_{\text{Bragg}} + 1°$.

To conclude, we believe that the use of appropriate anomalous scattering factors is mandatory in the data analysis of [1]. Therefore to us and on the basis of the results presented in [1], the authors have not conveniently proved that the fully charged zigzag model 1 is the actual charge ordering present in α'-NaV_2O_5. At the level of accuracy of the present anomalous scattering factors' data, both zigzag models equally reproduced their experimental data (only one meaningful reflection has been measured).

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Received 6 March 2001; published 10 October 2001
DOI: 10.1103/PhysRevLett.87.189702
PACS numbers: 71.27.+a, 61.10.Eq, 75.10.Jm

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